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Supplementary Information for Microwave-Assisted Hydrothermal Selective Dissolution and Utilisation of Hemicellulose in *Phyllostachys heterocycla cv. pubescens*

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I. MICROWAVE HYDROTHERMAL CONVERSION OF *PUBESCENS*

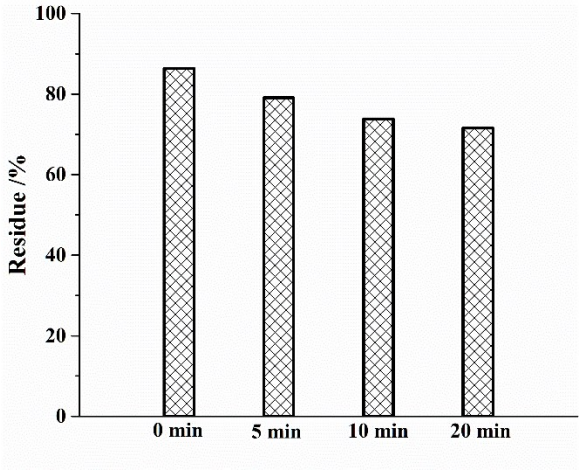

Figure S1 The variation of residue content with microwave hydrothermal treatment at 180 °C for different time

II. ^{13}C CPMAS NMR ANALYSIS

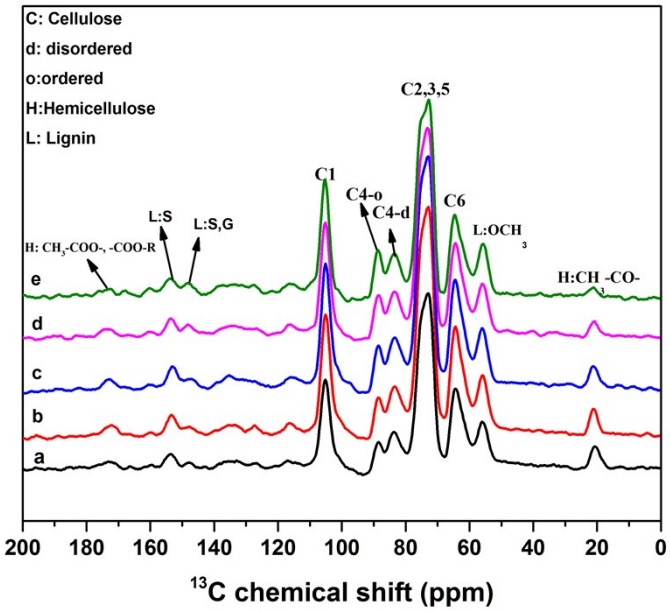

Figure S2 ^{13}C CPMAS solid-state NMR spectra of *pubescens* and solid samples after different treatment: a, *pubescens*; b, Residue 140 °C; c, Residue 160 °C; d, Residue 180 °C; e, Residue 200 °C. (Resonance assignment of ^{13}C CPMAS spectra was given in Table S1)

Table S1 Resonance assignment of ^{13}C CPMAS spectra of bamboo and reaction residue give in Figure S2.

Resonance number	Chemical shift (ppm)	Assignment
1	171	Hemicellulose: -COO-R, CH_3-COO-
2	153	Lignin: $S_{3(e)}$, $S_{5(e)}$
3	147	Lignin: $S_{3(ne)}$, $S_{5(ne)}$, $G_{3(ne,\ e)}$, $G_{4(ne,\ e)}$
4	104	Cellulose: C_1
5	88	Cellulose: C_4 (ordered)
6	83	Cellulose: C_4 (disordered)
7	74-72	Cellulose: C_2, C_3, C_5
8	64	Cellulose: C_6 (ordered), C_6 (disordered)
9	56	Lignin: OCH_3
10	21	Hemicellulose: CH_3-COO-

III. SEM ANALYSIS

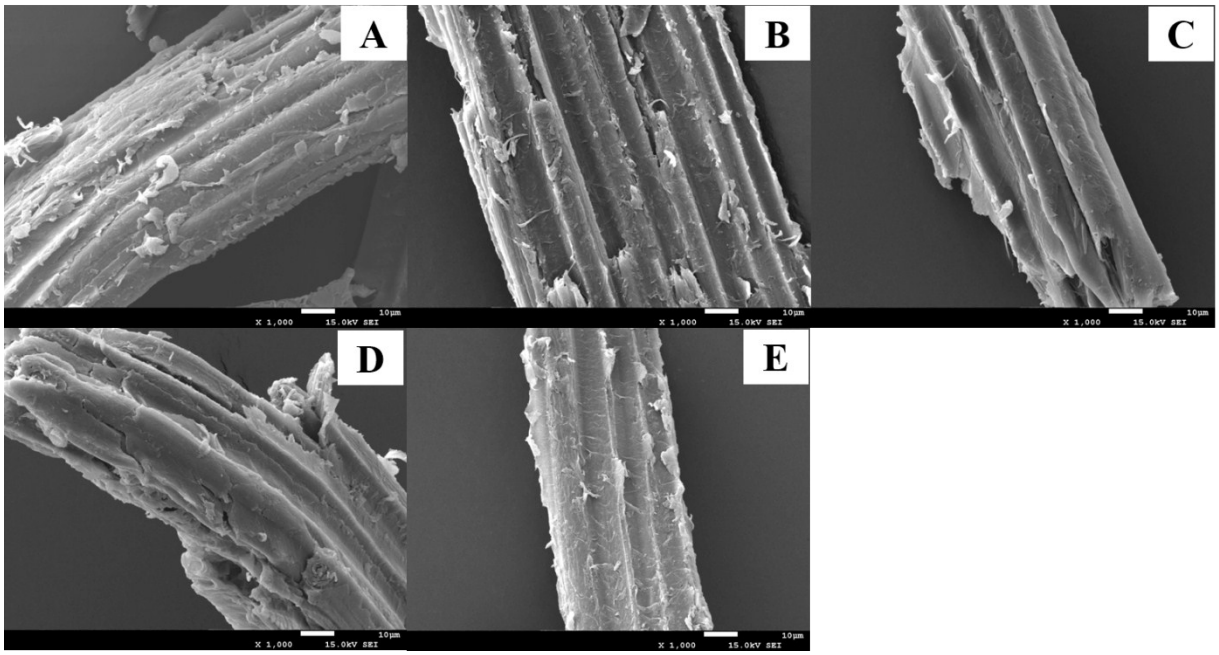

Figure S3 SEM micrographs of *pubescens* feedstock and solid residues obtained with microwave hydrothermal treatment at different temperature: (A) *pubescens* feedstock; (B) 140 °C; (C) 160 °C; (D) 180 °C; (D) 190 °C.

IV. THERMOGRAVIMETRY ANALYSIS

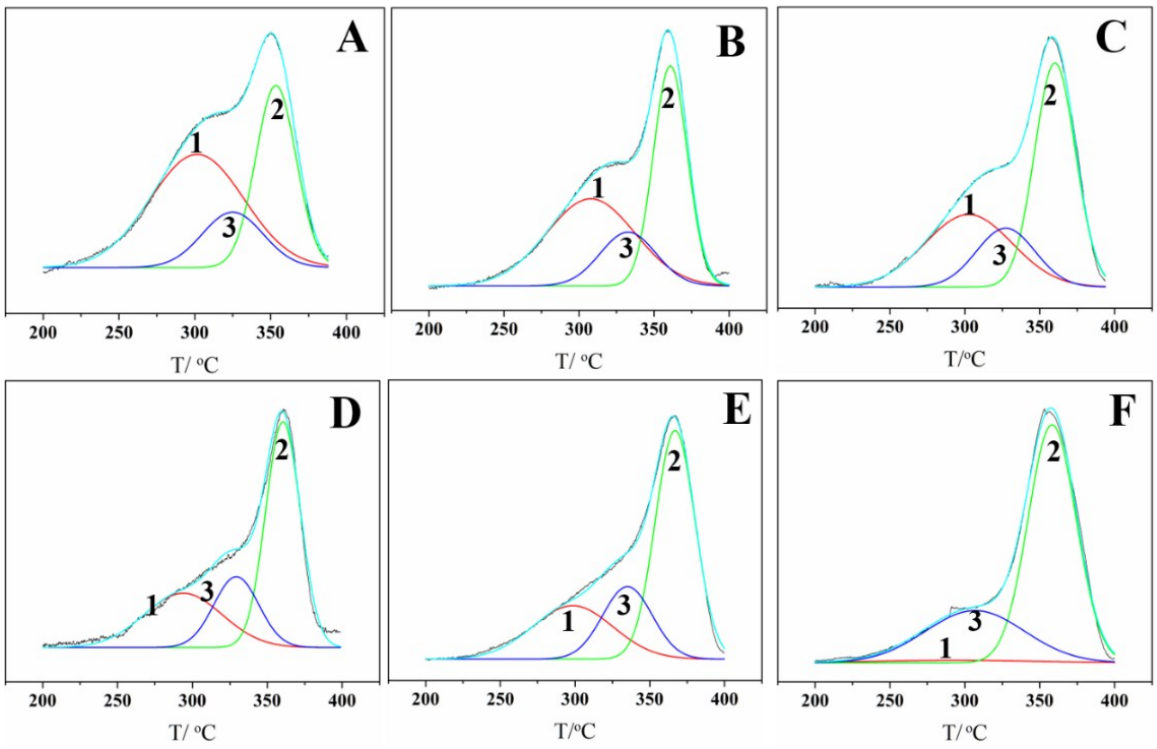

Figure S4 Fitted DTG curves of hemicellulose, cellulose and lignin components in *pubescens* feedstock and solid residues obtained with microwave hydrothermal treatment at different temperature: (A) *pubescens*; (B) 140 °C; (C) 160 °C; (D) 180 °C; (E) 190 °C; (F) 200 °C.

V. PY-GC/MS ANALYSIS

The pyrolysis compounds were identified in the NIST computer libraries. Semi-quantification was based on the peak areas, considering the total peak area as 100%. The relative peak area of individual product was calculated by dividing the total areas of all the peaks. The syringyl/guaiacyl(S/G) ratio was calculated by dividing the sum of syringyl units peak areas by the sum of guaiacyl units peak areas. The identification and relative peak area of the compounds released after Py-GC/MS of *pubescens*, and residues with microwave treatment at 200 °C were shown in Table S2.

Table S2 The pyrolysis products released after Py-GC/MS of *pubescens* and residues with microwave treatment at 200 °C

No.	R.T.(min)	Compound name	Relative area / %	
			Pubescens	Residues at 200 °C
Lignin guaiacyl-type				
1	9.533	Phenol, 2-methoxy-	1.26	1.63
2	11.134	Creosol	0.75	1.19
3	12.882	2-Methoxy-4-vinylphenol	3.79	3.76
4	13.477	Phenol, 2-methoxy-5-(1-propenyl)-, (E)-	0.87	0.46
5	14.037	Vanillin, acetate	0.76	0.92
6	14.140	Phenol, 2-methoxy-5-(1-propenyl)-, (E)-	0.24	-
7	14.620	1,2,4-Trimethoxybenzene	1.93	4.58
8	14.677	Phenol, 2-methoxy-5-(1-propenyl)-, (E)-	1.31	-
9	15.157	p-Cymene-2,5-diol	0.41	0.43
Sum			11.32	12.97
Lignin syringyl-type				
10	13.374	Phenol, 2,6-dimethoxy-	5.10	6.17
11	15.614	2,5-Dimethoxybenzoic acid	0.45	0.92
12	16.094	2',4'-Dimethoxyacetophenone	4.18	4.10
13	16.528	(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol	0.92	1.16
14	17.1	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.78	0.77
15	17.203	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	1.38	2.34
16	17.443	2-Allyl-1,4-dimethoxy-3-methyl-benzene	0.65	0.70
17	17.66	(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol	3.99	4.46
18	18.037	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	1.35	1.37
19	18.151	(E)-4-(3-Hydroxyprop-1-en-1-yl)-2-methoxyphenol	0.18	0.44
20	18.426	3,5-Dimethoxy-4-hydroxyphenylacetic acid	2.00	1.20
21	20.574	3,5-Dimethoxy-4-hydroxycinnamaldehyde	1.09	1.15
22	20.986	trans-Sinapyl alcohol	1.17	1.14
Sum			23.23	25.92
S/G			**2.05**	**2.00**

VI. MICROWAVE-ASSISTED TREATMENT OF SOFTWOOD AND WHEAT STRAW

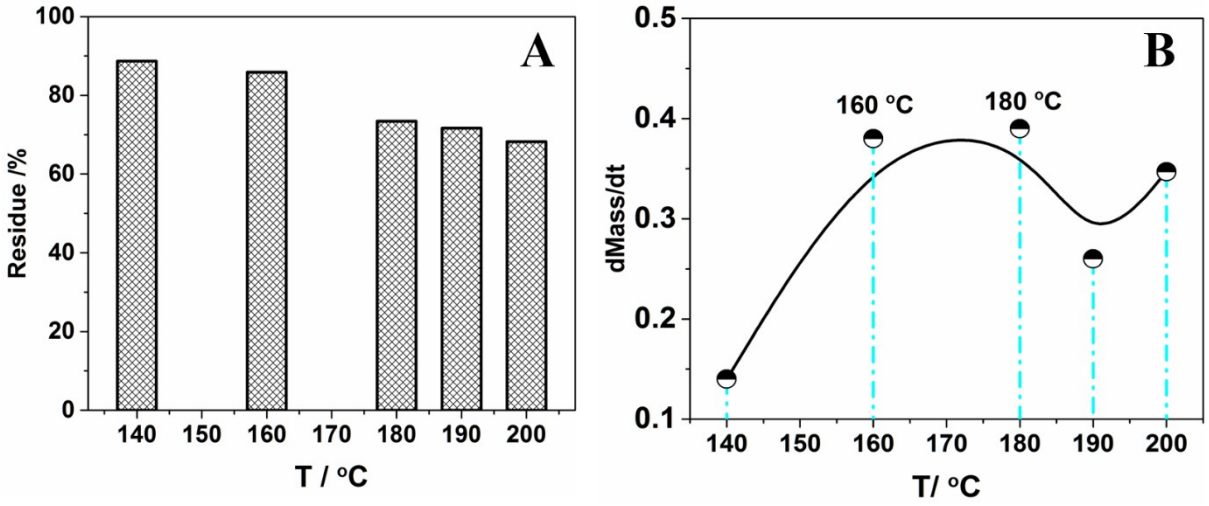

Figure S5 Microwave-assisted hydrothermal conversion of softwood with holding time of 5 min:(A) The variation of residue content with microwave treatment at different temperatures; (B) The effect of temperature on the mass loss rate of softwood.

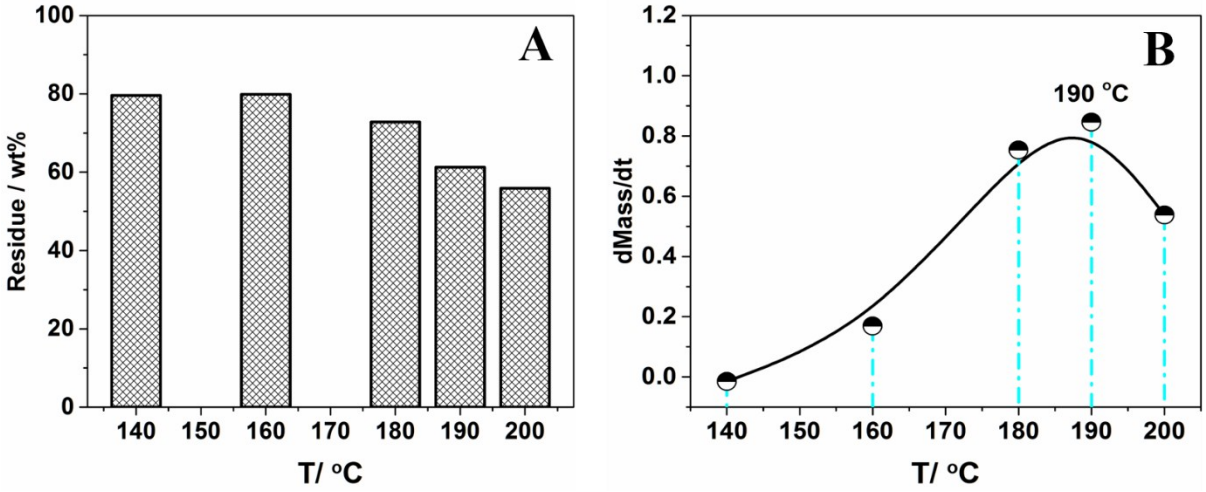

Figure S6 Microwave-assisted hydrothermal conversion of wheat straw with holding time of 5 min:(A) The variation of residue content with microwave treatment at different temperatures; (B) The effect of temperature on the mass loss rate of wheat straw.

VII. THERMOGRAVIMETRIC ANALYSIS RESULTS OF SOFTWOOD AND WHEAT STRAW

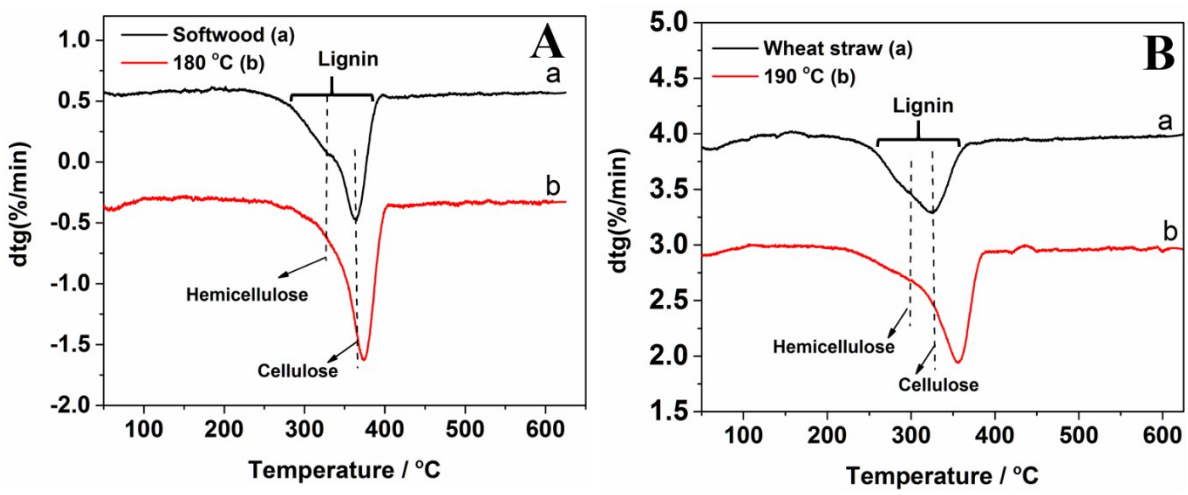

Figure S7 The DTG curves of softwood (A) and wheat straw (B) by thermogravimetric analysis.

VI. ^{13}C NMR ANALYSIS

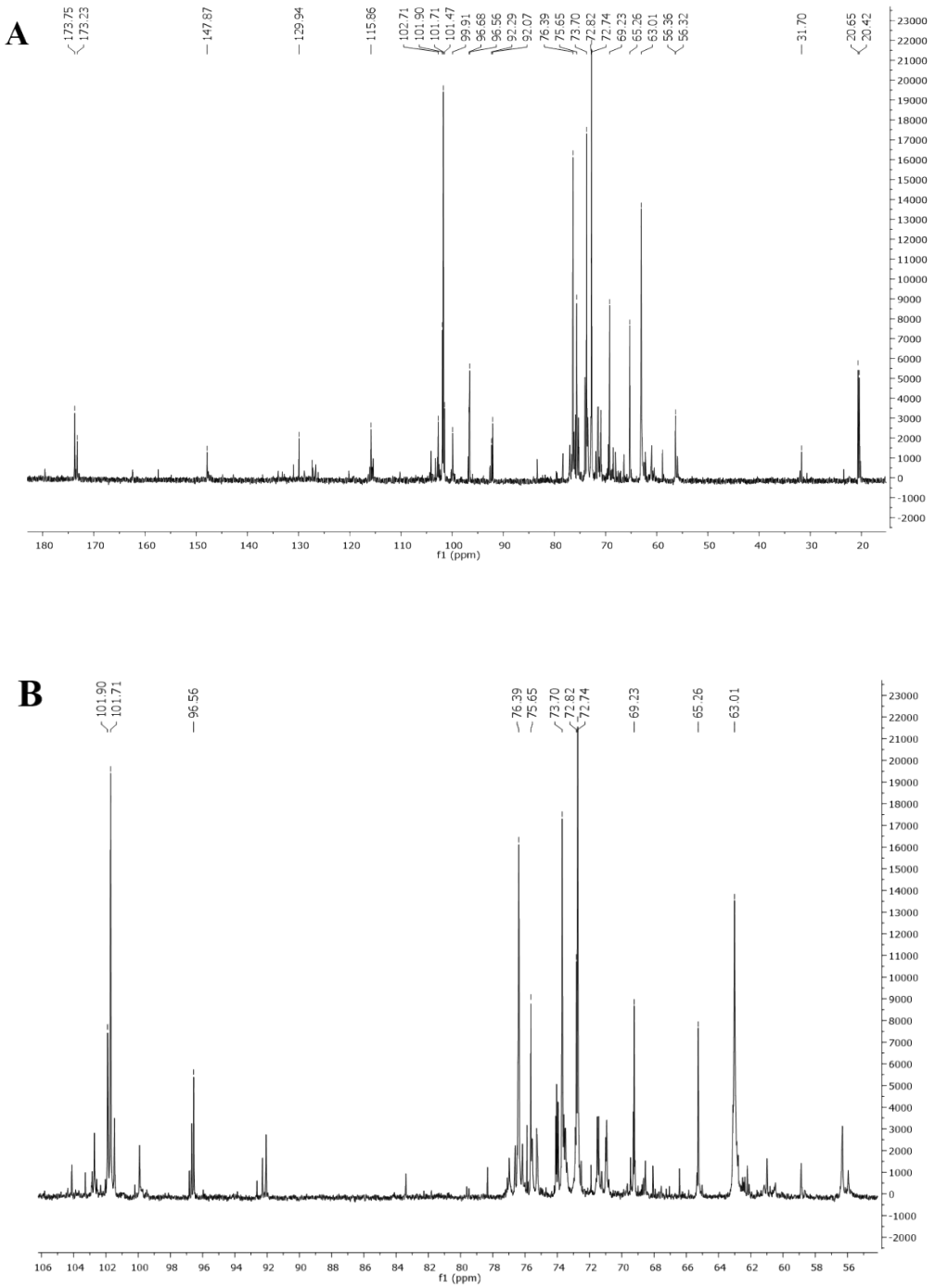

Figure S8 ^{13}C NMR results of hydrolysate obtained with microwave hydrothermal treatment at 200 ^{o}C:(A) chemical shifts from 10-180 ppm; (B) chemical shifts from 54-106 ppm

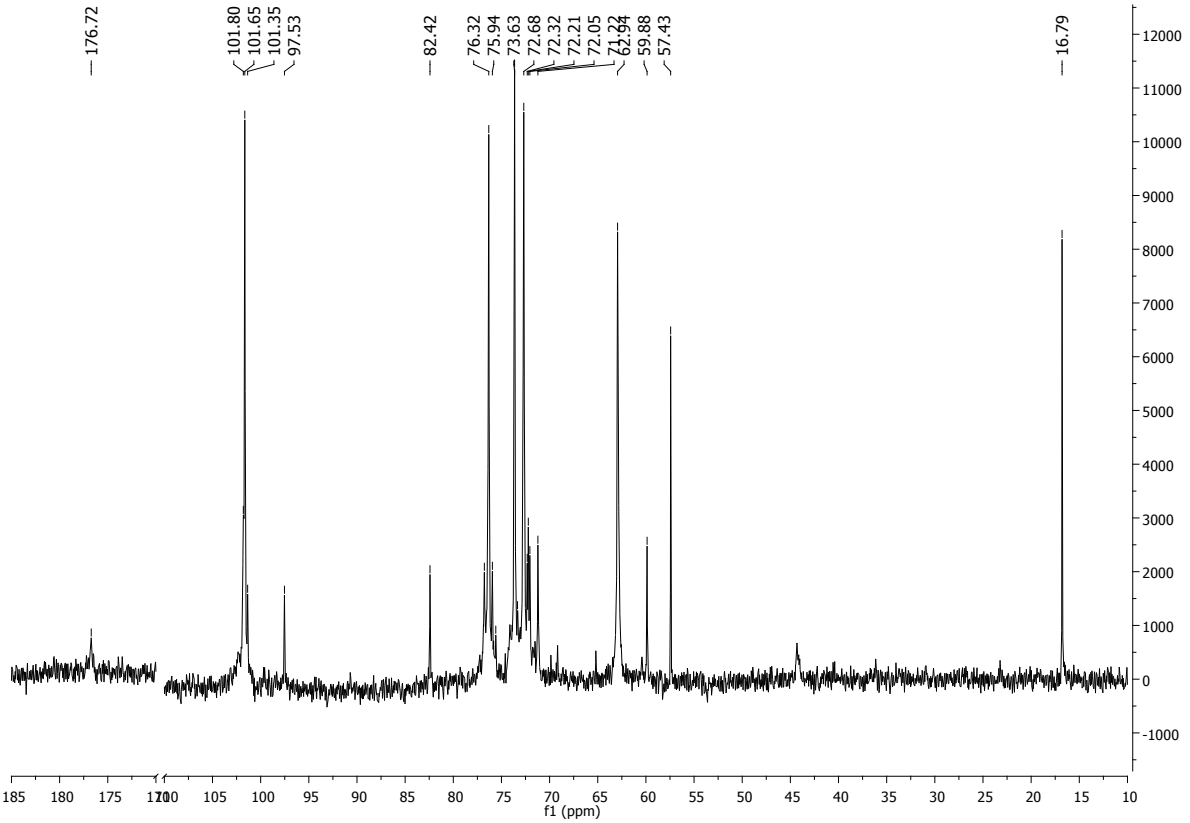

Figure S9 ^{13}C NMR spectra of xylan from birch wood in D_2O

IX. 2D HSQC NMR ANALYSIS

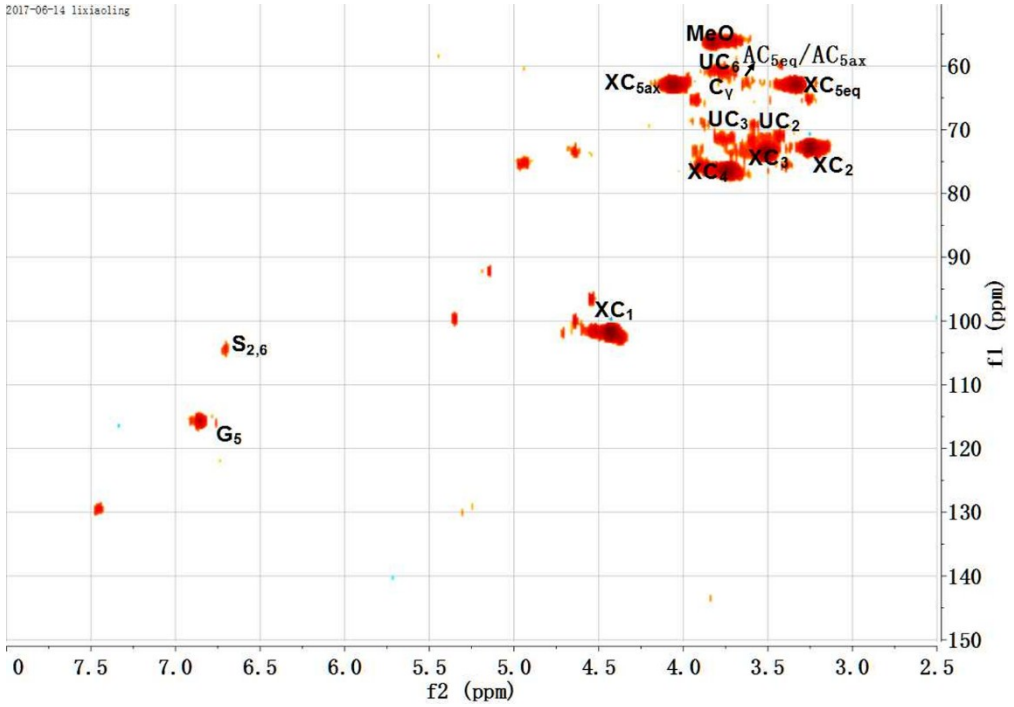

Figure S10 2D HSQC NMR spectra of the liquid fraction obtained with microwave treatment at 200 °C

Table S3 Assignment of main hemicellulose and lignin ^{13}C-^{1}H correlation signals in HSQC spectra of liquid fraction[1]

Lables	δ_C/δ_H	Assignment
MeO	56.0/3.71	C-H in methoxyls
X_{C1}	102.4/4.33	C-1 in β-D-xylp
X_{C2}	73.3/3.21	C-2 in β-D-xylp
X_{C3}	73.9/3.40	C-3 in β-D-xylp
X_{C4}	75.9/3.66	C-4 in β-D-xylp
X_{C5eq}	63.3/3.27	C-5eq in β-D-xylp, (eq) equatorial
X_{C5ax}	63.3/3.96	C-5ax in β-D-xylp, (ax) axial
A_{C5eq}/A_{C5ax}	61.7/3.58	C-5eq/C-5ax in α-L-Araf, (eq) equatorial/(ax) axial
U_{C2}	71.7/3.46	C-2 in α-D-GlcpA
U_{C3}	73.4/3.68	C-3 in α-D-GlcpA
U_{C6}	59.9/3.76	C-6 in α-D-GlcpA
C_γ	62.7/3.73	C_γ-H_γ in β-5’ structures (C)
$S_{2,6}$	104.4/6.72	$C_{2,6}$-$H_{2,6}$ in syringyl units (S)
G_5	114.9-115.9/6.75	C_5-H_5 in guaiacyl units (G)

The results showed that the main hemicellulose signals correspond to C-1, C-2, C-3, C-4, C-5eq and C-5ax of β-D-xylp were observed. While some signals of side chains assigned to C-5eq/C-5ax of α-L-Araf, C-2, C-3 and C-6 of α-D-GlcpA were observed with weak intensity. The main lignin ^{13}C-^{1}H correlation signals in side-chain region (δ_C/δ_H 50-103/2.6-6.0 ppm) and in the aromatic region (δ_C/δ_H 103-145/6.0-8.0 ppm) for the HSQC spectra of liquid fraction were weak, only OCH_3, $S_{2,6}$ (correspond to $C_{2,6}$-$H_{2,6}$ in syringyl units) and G5 (C_5-H_5 in guaiacyl units) signals in lignin were observed in 2D HSQC spectra. The results suggested that most lignin retained in the solid residue after microwave hydrothermal treatment at 200 ^{o}C, which were consisted with Py-GC/MS results (Table S2). This further confirmed that the efficient extraction of hemicellulose with microwave treatment at 200 ^{o}C was achieved.

References

1. D. Yang, L. X. Zhong, T. Q. Yuan, X. W. Peng, R. C. Sun, *Ind. Crops Prod.,* 2013, ***43***, 141

